

LETTER TO THE EDITOR

Theory of coagulation in charged colloidal suspensions

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Abstract. A theory of the coagulation rate in concentrated suspensions of Brownian particles, interacting via the familiar Derjaguin–Landau–Verwey–Overbeek (DLVO) pair potential, is proposed. An effective pair potential between two coagulating particles is obtained by thermally averaging over the fluctuating cage of neighbouring particles and thereby the problem can be treated within a modified Smoluchowski–Debye approach. Testing the theory against extensive Brownian dynamics computer simulations, reasonable agreement is found.

The Coulomb barrier between two highly charged colloidal particles normally prevents them from irreversible coagulation due to the strong van der Waals attraction. The height of this potential barrier, however, can easily be controlled by the amount of added salt and therefore coagulation can be seen on experimentally accessible time-scales. A calculation of the coagulation rate is therefore very important from both a principle and a technical point of view in order to estimate the time for which the suspension remains stable. Indeed the first study dates back to the very beginning of colloid history when von Smoluchowski [1] used a simple model of noninteracting sticky spheres to predict the rate of diffusion-limited aggregation. His approach was generalized to two particles with an arbitrary interaction (reaction-limited coagulation) by Debye [2] (see also the textbook of Verwey and Overbeek [3]). More recent work for the coagulation rate concerns the inclusion of hydrodynamic interactions [4, 5] as well as analytical expansions [6] and detailed experimental investigations [7, 8]; a recent comprehensive review can be found in the textbook of Russel *et al* [9].

In all the former works, basically the rate between two particles is calculated neglecting all the neighbouring particles. This approximation is of course excellent in the limit of high dilution where the interparticle forces are small for the mean interparticle distance. In this letter we address the question of how the rate is affected by the neighbouring particles, which is of peculiar importance for *concentrated* or *strongly interacting* colloidal suspensions. The model we use consists of Brownian particles interacting via the Derjaguin–Landau–Verwey–Overbeek (DLVO) potential [3, 10]. The aim of the letter is twofold. First we present a simple theory for the coagulation rate, whose basic idea was also applied in the context of reaction rates in dense plasmas [11]: an effective pair potential between a pair of coagulating particles is obtained by thermally averaging over all neighbouring particles and then the Smoluchowski–Debye approach is taken for this effective potential. Second, we present extensive Brownian dynamics computer simulations to obtain ‘exact results’ within our model in order to check the theory.

Let us first describe briefly the model. For a given temperature T and particle concentration ρ we are considering Brownian particles characterized by a short-time self-diffusion constant D_0 which are interacting via the DLVO pair potential $V_{DLVO}(r) = V_{el}(r) + V_{vdW}(r) + V_{hc}(r)$ where r is the interparticle distance. The screened electrostatic repulsion is contained in the Yukawa potential $V_{el}(r) = Z^2 \exp(-\kappa(r - \sigma))/4\pi\epsilon_0\epsilon r(1 + \kappa\sigma/2)^2$, where Z is the macroion charge, $\epsilon_0\epsilon$ the dielectric constant of the solvent, σ the particle diameter and κ the Debye–Hückel screening constant. Note that many-body forces resulting from nonlinear screening can also be embodied into a pairwise Yukawa potential [12], where the actual Yukawa parameters, however, differ in general from the DLVO expressions. Hence the assumption of a pairwise Yukawa potential is justified also for higher concentrations. The attraction induced by the van der Waals forces is given by $V_{vdW}(r) = -(A/6)\{\sigma^2/2(r^2 - \sigma^2) + \sigma^2/2r^2 + \ln(1 - \sigma^2/r^2)\}$ where the Hamaker constant A sets the energy scale. Finally the hard-core potential $V_{hc}(r)$ describes the excluded-volume interaction of two spheres with diameter σ . A typical shape of the DLVO potential is depicted in figure 1 (full line), exhibiting the Coulomb barrier and the van der Waals divergence near contact. For a stable suspension, all interparticle distances are larger than the position of the Coulomb barrier. If two particles can overcome the barrier by Brownian motion, they will be attracted by the van der Waals divergence and stick together, forming a coagulated pair.

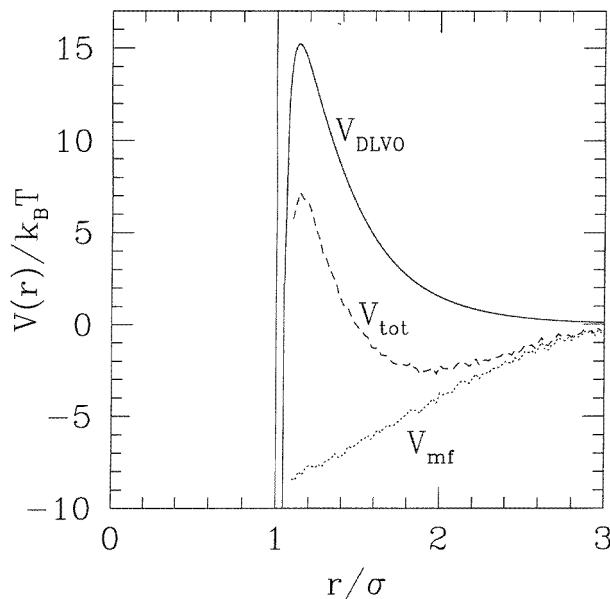


Figure 1. Different interparticle potentials, $V(r)$, in units of $k_B T$ versus reduced interparticle distance r/σ : DLVO potential $V_{DLVO}(r)$ (full line), mean-field potential energy $V_{mf}(r)$ (dotted line), and total effective potential $V_{tot}(r)$ (dashed line). The two latter quantities are gained by Monte Carlo simulations; the small irregularities in $V_{mf}(r)$ and $V_{tot}(r)$ are due to statistical errors. The parameters are $A = 50k_B T$, $\sigma = 51$ nm, $\kappa\sigma = 2.37$, $\rho\sigma^3 = 0.1527$, $T = 300$ K, $Z = 105 e$, and $\epsilon = 78$, corresponding to typical values of aqueous charged suspensions.

Consider now two particles that are nearly coagulated, i.e. that possess an interparticle distance $r = R$ slightly larger than the position of the barrier. They feel both their direct interaction as well as the influence of the fluctuating cage of neighbour particles. The latter

influence can be incorporated into an effective pair potential between two such particles by canonically averaging over the cage. In order to perform this average the two particles are considered to be fixed. Then the remaining particles exhibit a one-particle density profile $\rho(\mathbf{r}, R)$ around the two particles, which depends parametrically on R . We define this quantity as static equilibrium property for a stable ‘substitute’ system without any coagulated pairs, i.e. for an ensemble characterized by a pair potential that is infinity for distances smaller than the position of the barrier. Such a density profile clearly involves triplet correlations of the bulk fluid and is readily accessible either by computer simulation or by density functional theory. Due to the average over the fast fluctuations of the neighbour particles, the resulting potential energy is obtained in a ‘mean-field’-like approximation

$$V_{mf}(R) = \int d^3r [V_{DLVO}(r) + V_{DLVO}(|\mathbf{r} - R\mathbf{e}_x|)]\rho(\mathbf{r}, R) - 2V_0 \quad (1)$$

where \mathbf{e}_x denotes a unit vector and the constant V_0 is the potential energy of one tagged particle in the fluid of the other particles. The total effective interaction between two coagulating particles is $V_{tot}(r) = V_{DLVO}(r) + V_{mf}(r)$. Typical shapes of $V_{mf}(r)$ and $V_{tot}(r)$ as gained by Monte Carlo computer simulations are shown in figure 1 (dotted and broken lines). For a noninteracting system, $\rho(\mathbf{r}, R) = \rho = \text{constant}$ and $V_{mf}(r) = \text{constant}$ and hence $V_{tot}(r)$ coincides with $V_{DLVO}(r)$ up to an irrelevant constant. In concentrated or highly interacting suspensions, however, due to strong correlations of macroions, $V_{mf}(r)$ is attractive, thus reducing the barrier in the total potential with respect to the bare DLVO interaction (see again figure 1).

Starting from the total effective potential we now have to find the coagulation rate. In the limit of high dilution, the Smoluchowski–Debye theory [9] yields a rate per particle, $\gamma \equiv \Gamma/N$, to reach an interparticle distance R_b in terms of the interparticle potential $U(r)$ as follows:

$$\gamma \equiv \gamma[U(r)] = 8\pi D_0 \rho \left(\int_{R_b}^{\infty} dr [\exp(U(r)/k_B T)]/r^2 \right)^{-1} \quad (2)$$

where k_B is Boltzmann’s constant. Let us define the coagulation time τ as the mean time a particle needs to reach the barrier height, i.e. $\tau = 1/\gamma$. In the traditional Smoluchowski–Debye theory, this time is simply obtained as $\tau \equiv \tau_{DLVO} := 1/\gamma[V_{DLVO}(r)]$. Data are given in table 1 for two different DLVO-type potentials: both of them correspond to a fluid phase of macroions. It seems to be quite natural to define a different coagulation time by using the total effective potential in the Smoluchowski–Debye expression (2), i.e. $\tau_{tot} := 1/\gamma[V_{tot}(r)]$. Data for τ_{tot} are also collected in table 1. They are considerably smaller than τ_{DLVO} due to the reduction of the barrier height in $V_{tot}(r)$. In doing this, however, one has overlooked the important fact that $V_{tot}(r)$ has an attractive well (see again figure 1) and the particles on average start from a distance corresponding to a position in the attractive well. Interestingly enough this again enhances the effective barrier felt by the particles. For a concentrated suspension, only the limited range of interparticle distances r with $R_b < r < r_0$ is physical, where r_0 is a typical interparticle spacing. We define r_0 as a minimal averaged interparticle distance via the equation

$$4\pi\rho \int_0^{r_0} dr' r'^2 g(r') = 1. \quad (3)$$

Here $g(r)$ is the equilibrium pair correlation function of the ‘substitute’ system stabilized against coagulation by setting the interparticle potential to infinity for interparticle distances smaller than the position of the barrier. The zero point of the potential now has to be chosen

such that the potential vanishes for $r = r_0$. Shifting the potential by a constant we finally find within this modified Smoluchowski–Debye theory for the coagulation time

$$\tau \equiv \tau_{mf} = \frac{1}{8\pi D_0 \rho} \int_{R_b}^{r_0} dr \frac{1}{r^2} \exp[(V_{tot}(r) - V_{tot}(r_0))/k_B T] \quad (4)$$

data of which are again shown in table 1. As expected, $\tau_{mf} > \tau_{tot}$. In (4), which is the basic theoretical result of our investigations, the rate of a non-equilibrium process is expressed in terms of static pair and triplet equilibrium correlations of a ‘substitute’ system stabilized against coagulation as embodied in the quantities $g(r)$ and $\rho(r, R)$. We finally remark that the true physical coagulation rate is again reduced by a factor of one-half since the particles have a probability of one-half of falling back into the dissociated state from the barrier maximum.

Table 1. Mean coagulation time in units of the Brownian relaxation time $\tau_B \equiv \sigma^2/6D_0$ for two different combinations of parameters: (a) as in figure 1; (b) as in figure 1 but with $A = 500k_B T$, $\kappa\sigma = 4.91$, $\rho\sigma^3 = 0.1909$, and $Z = 300 e$. The results from different theories, τ_{DLVO} , τ_{tot} , and τ_{mf} are given as well as the exact data, τ , from Brownian dynamics simulations. For the latter data, the statistical error is indicated. For completeness, the position R_b/σ of the barrier, its height $\Delta U/k_B T$, and the initial distance r_0/σ are also given.

| | R_b/σ | $\Delta U/k_B T$ | r_0/σ | τ_{DLVO}/τ_B | τ_{tot}/τ_B | τ_{mf}/τ_B | τ/τ_B |
|-----|--------------|------------------|--------------|----------------------|---------------------|--------------------|---------------|
| (a) | 1.138 | 15.20 | 1.69 | 247 000 | 92 | 567 | 467 ± 35 |
| (b) | 1.246 | 9.42 | 1.63 | 533 | 40 | 41 | 30 ± 2 |

We have also performed Brownian dynamics computer simulations in order to obtain exact data for the mean coagulation time per particle. The standard simulation scheme [13] is used involving a cubic simulation box with periodic boundary conditions. The simulations are nontrivial insofar as the time-step has to be very small (for more details see [14]). We start from an ensemble of equilibrated configurations of the ‘substitute’ system stabilized against coagulation and measure then the time it takes until the interparticle distance is equal to the barrier position. Averaging over typically 500 starting configurations, we obtain the mean coagulation time. In order to check that the rate per particle scales with the system size and in order to perform a finite-size analysis, we have performed runs of different system sizes ranging from $N = 108$ to $N = 1372$ particles. The results for the mean coagulation time per particle are shown in figure 2, exhibiting a clear saturation within the statistical error for $N \gtrsim 200$. This means that finite-size effects are relatively unimportant as long as systems of this size are used. It also implies that the rate scales with N , which we anticipated in our theory.

The exact simulation data for two different DLVO potentials are also given in table 1. In comparing them with our theoretical results one obtains fair agreement, keeping in mind that the coagulation rate is rather sensitive with respect to details of the barrier. In general the coagulation time is overestimated by theory by less than 40%. This can be understood qualitatively as follows. The rate is enhanced by rare favourable fluctuations reducing the barrier in the instantaneous effective potential energy between two nearly touching particles. Since we have averaged over any fluctuations, our mean-field barrier is a little too high. However, a theory including this effect is much more difficult since it requires a detailed knowledge of rare fluctuations. It is surprising that the naive Smoluchowski–Debye expression with the total potential $V_{tot}(r)$ yields coagulation times that can be smaller or larger than the exact values, showing that the effect of an enhanced barrier at averaged

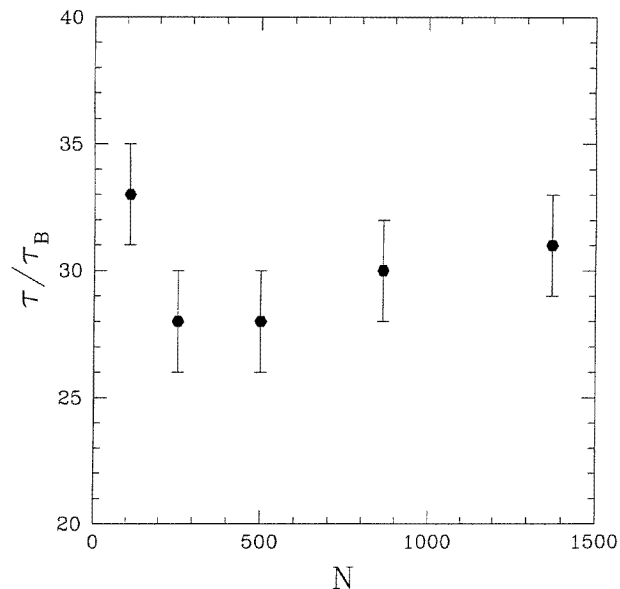


Figure 2. Mean coagulation time per particle, τ , in units of τ_B as obtained by Brownian dynamics computer simulations, versus number of particles N in the simulation box. The bars indicate the statistical error of the simulation due to the finite number of starting configurations. The parameters are as in case (b) of table 1.

nearest-neighbour distance induced by particle correlations is a delicate one. For the parameter combination (b), the results for τ_{tot} are in accordance with the simulation while they fail completely in case (a). Moreover, the DLVO-based coagulation times, τ_{DLVO} , are much too high (see again table 1). Consequently both the influence of correlational effects and that from a different starting position have to be taken into account in constructing a coagulation rate theory of strongly interacting suspensions.

In conclusion we have shown that structural correlations in concentrated suspensions can significantly enhance the coagulation rate with respect to the bare coagulation rate based on the direct pair interaction. By introducing an effective pair potential between two coagulating particles which contains correlations, the effective barrier is suppressed. A rate can be gained by using a modified Smoluchowski–Debye theory, yielding satisfying agreement with the exact data based on Brownian dynamics simulations.

We finish with a couple of remarks. First, in our simple model, any hydrodynamic interactions between the colloidal particles mediated by the solvent are neglected. For strongly interacting charged suspensions, however, the volume fraction is typically small, which implies that hydrodynamic interactions are only important for two nearly touching coagulating particles, while a computer simulation of hydrodynamic interactions requires a tremendous effort [15] and it is still not possible to simulate rare events such as coagulation processes on present-day computers. In the theory, the pairwise hydrodynamic interaction can be incorporated by replacing $1/r^2$ with $1/r^2 G(r)$ in the right hand-side of (2) and (4). Here $G(r)$ is a known hydrodynamic function [9] diverging at contact. Second, the validity of the Yukawa expression for the electrostatic part in the DLVO potential near contact can be questioned. One should use more sophisticated density-functional schemes [16] to check how much the Coulomb barrier is reduced by nonlinear counterion screening. Finally, we

would like to mention that coagulation may also provide an effective channel to melt a colloidal crystal. A coagulated particle pair is a defect in the crystal and upon a finite defect concentration *coagulation-induced melting* of the crystal may take place. We are at present performing further computer simulations to explore details of this effect.

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